



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |  |  |   |
|--|--|--|---|
| (51) International Patent Classification <sup>4</sup> :<br><br>A01N 43/50, 25/30, 25/00  |  | A1   | (11) International Publication Number: <b>WO 88/02987</b><br><br>(43) International Publication Date: 5 May 1988 (05.05.88) |
| <p>(21) International Application Number: PCT/US87/02257</p> <p>(22) International Filing Date: 8 September 1987 (08.09.87)</p> <p>(31) Priority Application Number: 925,321</p> <p>(32) Priority Date: 31 October 1986 (31.10.86)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: GREAT LAKES CHEMICAL CORPORATION [US/US]; Highway 52 N.W., P.O. Box 2200, West Lafayette, IN 47906 (US).</p> <p>(72) Inventor: SMITH, Roger, E. ; Highway 52 N.W., P.O. Box 2200, West Lafayette, IN 47906 (US).</p> <p>(74) Agents: Roedel, John, K. et al.; Senniger, Powers, Leavitt &amp; Roedel, 611 Olive Street, Suite 2050, St. Louis, MO 63101 (US).</p> |  | <p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, RO, SE (European patent), SU.</p> <p><b>Published</b><br/><i>With international search report.<br/>With amended claims.</i></p> |   |

(54) Title: METHOD FOR CONTROLLING PLANT DISEASES AND MICROORGANISMS IN THE PRESENCE OF PLANTS

(57) Abstract

Novel method for controlling the growth of microorganisms on, in or near plants. More particularly, in one embodiment, growth of microorganisms is controlled on a surface that is in such proximity to a higher order plant that contacting such surface with a stream of water may cause liquid water from the stream to be deflected and contact the higher order plant or the growth medium in which it is rooted. In this embodiment, an N-halohydantoin is incorporated in water to produce treated water having an N-halohydantoin concentration sufficient to inhibit the growth of microorganisms in the water or on a substrate to which the treated water is applied. Then the surface is contacted with the treated water, thereby inhibiting the growth of microorganisms on the surface, without harming the higher order plant by contact with the N-halohydantoin contained in any of the treated water that may contact the plant or the growth medium in which said plant is rooted. In other embodiments, plants, fruit, vegetables, seeds, plant bulbs, or the medium in which plants, seeds or bulbs are implanted may be treated with N-halohydantoin to control plant disease or unwanted microorganisms without harming the plants, fruit, seeds or plant bulbs.

**BEST AVAILABLE COPY**

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT:

|    |                              |    |  |    |                          |
|----|------------------------------|----|--|----|--------------------------|
| AT | Austria                      | FR | France                                   | ML | Malta                    |
| AU | Australia                    | GA | Gabon                                    | MR | Mauritania               |
| BB | Barbados                     | GB | United Kingdom                           | MW | Malawi                   |
| BE | Belgium                      | HU | Hungary                                  | NL | Netherlands              |
| BG | Bulgaria                     | IT | Italy                                    | NO | Norway                   |
| BJ | Benin                        | JP | Japan                                    | RO | Romania                  |
| BR | Brazil                       | KP | Democratic People's Republic<br>of Korea | SD | Sudan                    |
| CF | Central African Republic     | KR | Republic of Korea                        | SE | Sweden                   |
| CG | Congo                        | LI | Liechtenstein                            | SN | Senegal                  |
| CH | Switzerland                  | LK | Sri Lanka                                | SU | Soviet Union             |
| CM | Cameroon                     | LU | Luxembourg                               | TD | Chad                     |
| DE | Germany, Federal Republic of | MC | Monaco                                   | TG | Togo                     |
| DK | Denmark                      | MG | Madagascar                               | US | United States of America |
| FI | Finland                      |    |  |    |                          |

METHOD FOR CONTROLLING PLANT DISEASES  
AND MICROORGANISMS IN THE PRESENCE OF PLANTS

Background of the Invention

This invention relates to plant diseases and  
5 deleterious microorganisms found in environments adapted  
for the growth of higher order plants, and more particu-  
larly to control and inhibition of plant diseases and  
deleterious microorganisms found in such environments.

In environments adapted for the growth of plants  
10 of higher biological development or complexity than micro-  
organisms such as bacteria, yeast, algae or simple fungus,  
that is, in environments adapted for the growth of higher  
order plants, development of such microorganisms on practi-  
cally any moist surface has been a longstanding and  
15 intractable problem.

Greenhouses contain a myriad of water sources,  
including irrigation water, irrigation water run-off,  
spilled water, cleaning water, condensation, atomized water  
drifting from a humidifier or evaporative cooler and  
20 extraneous sprayed water as might result from a water  
hose. Since almost all surfaces in a greenhouse tend to  
become moist from these sources, nearly any surface in a  
greenhouse may serve as a site for microorganism growth.  
Thus, in conventional greenhouses, microorganisms inevi-  
25 ably colonize and grow not only on the plants themselves,  
but also on all other surfaces such as walls, ceilings,  
floors, flower pots, flats, irrigation mats, irrigation  
equipment and evaporative cooling pads.

30 Similarly, in outdoor nurseries, crop fields, and  
any other environment, such as lawns or golf courses,

adapted for the growth of higher order plants, micro-organisms tend to develop on irrigation or sprinkling equipment, soil and the plants themselves, and containers and planters.

5       Growth of microorganisms often is deleterious to the operation of an irrigation system as well as to the higher order plants themselves. Growth of slime bacteria has a propensity to foul the system and clog irrigation equipment, reducing its efficiency. Likewise, development 10 of yeast, fungus and algae causes spoiling of plants, and the fruits and seeds of plants, and otherwise harms higher order plants. Development of pathogenic microorganisms such as *Verticillium*, *Pythium*, *Fusarium*, and *Pseudomonas* in or on plants also causes various plant diseases. Furthermore, 15 microorganism development in living plants may accelerate rotting or spoiling of the plants after harvesting, or even accelerate rotting or spoiling of fruits or seeds harvested from the plants. Moreover, development of micro-organisms in a greenhouse can cover the greenhouse with an 20 unappealing slime which rubs off on workers who brush against a coated greenhouse surface, blocks light transmission through the glass walls of the greenhouse, fouls the greenhouse, makes the greenhouse floors slippery, pro- 25 vide a breeding ground for fungus gnats and other pests, and potentially poses health hazards.

Previous attempts to inhibit microorganism development in plant environments either have failed or have been self-defeating because ordinary biocides or disinfectants, such as bleach or various quaternary ammonium 30 compounds, that have been employed to kill or inhibit microorganisms, also are toxic to the higher order plants in the environment. Thus, ordinarily the cleaning of

greenhouse surfaces has entailed tedious, labor intensive careful scrubbing of the surfaces to avoid accidentally contacting a plant with the biocide, or time consuming removal of all the higher order plants from the greenhouse 5 before washing down the surfaces with a hose. Moreover, it seems clear that because such biocides are phytotoxic, they cannot be considered for direct plant treatment either in the irrigation water to keep clean the surfaces contacted by the water, or in irrigation water or otherwise in order 10 to treat the plants themselves. On the other hand, however, while some biocides may have low enough phytotoxic characteristics to use directly on plants, many have been associated with health hazards to humans that eat the plants or harvested parts thereof.

15. In addition to the health hazards from the toxicity of the oxidizing biocides used in the prior art for treating microorganism development around plants, such biocides also usually involve other health hazards from some other characteristic, such as the explosiveness of 20 chlorine gas tanks. Other problems with many of the conventional chlorine biocides include instability of the biocide in the presence of organic matter, effectiveness of the biocide only in a narrow pH range, and the formation of chloramines in the presence of ammonia, thereby producing 25 residual compounds which undesirably persist in the environment. Further, the additives typically employed in irrigation systems for control of certain microorganisms, or for other purposes such as fertilization, tend to be compositions of high water solubility and so require 30 employment of expensive pumps and other mechanical parts to regulate the concentration of the additives, to maintain an appropriate concentration and to avoid a phytotoxic overdose.

As disclosed in Paterson U.S. patent 3,412,021 and Macchiarolo U.S. patent 4,297,224, 1-bromo-3-chloro-5,5-dimethylhydantoin is known as an oxidizing biocide for use in water treatment in certain environments, 5 such as swimming pools and cooling towers in which higher order plants are not a concern. Patent and other technical literature discloses a number of uses for this and other N-halohydantoin compounds based on the biocidal properties of these compounds.

10 Summary of the Invention

Among the several objects of the invention, therefore, may be noted the provision of a method for controlling unwanted microorganisms located on, in or near higher order plants without harming the higher order 15 plants; the provision of a method for cleaning greenhouses and surfaces therein with biocide treated water that does not harm higher order plants; the provision of a method for treating higher order plants for inhibition of unwanted microorganisms without harming the higher order plants; the 20 provision of a method for treating higher order plants for controlling disease to the plants without harming the plants; the provision of a method for treating higher order plants for inhibition of unwanted microorganisms and control of disease without harm to the plants and without the 25 need for extra pumps to apply the treatment; the provision of a method for treating harvested plants, fruits, vegetables, and seeds for inhibition of rotting or spoiling by treating growing plants; the provision of a method for irrigating plants whereby development of unwanted micro- 30 organisms is inhibited; the provision of a method for treating soil, growth media or aggregate, or hydroponic solutions for inhibiting unwanted microorganisms without

harming the plants; the provision of a method for treating an evaporative cooler or humidifier whereby development of unwanted microorganisms is inhibited; and the provision of a method for treating an evaporative cooler or humidifier 5 whereby development of unwanted microorganisms is inhibited, and plants contacted by atomized water emitted from the evaporative cooler or humidifier are unharmed.

Briefly, therefore, the present invention is directed to a novel method for controlling the growth of 10 microorganisms on a surface that is in such proximity to a higher order plant that contacting such surface with a stream of water may cause liquid water from the stream to be deflected and contact the higher order plant or the growth medium in which it is rooted. Also controls micro- 15 organisms in the root zone within the growth media. The method comprises incorporating an N-halohydantoin in water to produce treated water having an N-halohydantoin concentration sufficient to inhibit the growth of microorganisms in the water or on a substrate to which the treated water 20 is applied, and contacting the surface with the treated water, thereby inhibiting the growth of microorganisms on the surface. In the method, the higher order plant remains unharmed by the N-halohydantoin contained in any of the treated water that may contact the plant or the growth 25 medium in which the plant is rooted.

The present invention is also directed to a novel method for controlling growth of unwanted microorganisms on a surface whereby a higher order plant is not harmed, the surface being located in an environment for the growth of a 30 higher order plant. The method comprises incorporating N-halohydantoin in water to produce treated water having a concentration of N-halohydantoin sufficient to inhibit

growth of microorganisms, and contacting a surface with the treated water for controlling microorganisms thereon, the higher order plant being contacted with the treated water in connection with contacting the surface with the treated 5 water.

The present invention is further directed to a novel method for irrigating plants wherein growth of unwanted microorganisms on or in the plants is controlled without harming the plants. The method comprises incorporating N-halohydantoin in water to produce treated water having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms, and irrigating plants with the treated water. The present invention is also directed to such irrigation methods in which growth of 10 unwanted microorganisms in or on irrigation equipment and materials is controlled, and to such methods in which plant 15 disease is controlled without harming the plants.

The present invention is further directed to a novel method for controlling growth of disease or unwanted 20 microorganisms in a plant or a plant rhizosphere without harming the plant. The method comprises applying an N-halohydantoin to a growth medium in which the plant is rooted. The N-halohydantoin is dissolved in and conveyed to the rhizosphere by precipitation or irrigation water 25 received by the growth medium. The invention is also directed to such method wherein the N-halohydantoin is applied to a growth medium in which a seed or bulb for the plant are implanted.

The present invention is also drawn to a novel 30 method for controlling disease or growth of unwanted microorganisms in or on a plant without harming the plant. The

method comprises contacting the plant with an N-halohydantoin, preferably by dissolving N-halohydantoin in water to produce a disinfectant solution having a concentration of N-halohydantoin sufficient to inhibit growth of micro-  
5 organisms, and applying the disinfectant solution to said plant. Alternatively, a seed or bulb for the plants may be treated with N-halohydantoin.

The present invention is also drawn to a novel method for treating harvested plants whereby growth of  
10 unwanted microorganisms in or on the harvested plants is controlled without harming the plants. In the method, harvested plants are contacted with an N-halohydantoin. Preferably, N-halohydantoin is dissolved in water to produce a disinfectant solution having a concentration of  
15 N-halohydantoin sufficient to inhibit growth of micro-organisms. Then, the harvested plants are contacted with the disinfectant solution, whereby rotting or spoiling of the harvested plants is inhibited.

The present invention is further drawn to a novel  
20 method for production of harvested plants, fruit or seeds, or controlling disease in the plants, fruits, seeds, or vegetables, whereby growth of unwanted microorganisms in or on the vegetables, plants, fruit or seeds is controlled without harm to the vegetables, plants, fruit or seeds. In  
25 the method, growing plants are contacted with an N-halohydantoin and then the plants, or fruit or seeds from the plant are harvested. Preferably, the method comprises several steps. First, N-halohydantoin is dissolved in water to produce a disinfectant solution having a concentration of N-halohydantoin sufficient to inhibit growth of  
30 microorganisms. Then, growing plants are contacted with the disinfectant solution. Finally, the growing plants, or

their fruit or seeds are harvested and rotting or spoiling of the harvested plants is inhibited.

Description of the Preferred Embodiment

In accordance with the present invention, it has  
5 been discovered that N-halohydantoins, their metabolites  
and residuals, can be used for effective control of micro-  
organisms in a plant environment without risk of injury to  
higher order plants. More particularly it has been found  
that aqueous solutions of N-halohydantoins may be formu-  
10 lated in a wide easily attainable range of concentrations  
that are high enough to kill various unwanted micro-  
organisms such as slime bacteria, yeast, fungus and algae,  
yet low enough not to harm higher order plants, whether  
contact of the plant with the solution is intentional or  
15 incidental. Regulation of the concentration of N-halohy-  
dantoin is simplified by the relatively low solubility of  
these compounds in water, and the fact that the highest  
concentration of N-halohydantoin that is obtained under  
ordinary conditions is too low to result in phytotoxicity.  
20 Unexpectedly, not only is a saturated solution of N-halohy-  
dantoin harmless to plants but, astonishingly, actually  
seems to stimulate plant growth. It has further been found  
that solid state N-halohydantoins are not harmful to higher  
order plants, and that these biocides may thus be applied  
25 in either solid or solution form in plant environments, or  
indeed to the plants themselves, without risk of injury to  
plant systems or tissue.

Moreover, since ingestion of reasonable amounts  
of N-halohydantoins is not believed to pose health dangers  
30 to humans from toxicity, ingestion of plants or parts  
thereof treated with N-halohydantoin is believed to present

no serious or appreciable health risk. Further, since N-halohydantoins are neither flammable nor typically stored in pressurized containers, they do not present dangers from explosions. The N-halohydantoins of this invention also 5 show greater stability in the presence of organic matter and effectiveness over a wider pH range than shown by typical chlorine disinfectants of the prior art. Further, the N-halohydantoins of this invention do not tend to form chloramines in the presence of ammonia, and so are not 10 believed to form residual compounds which undesirably persist remain in the environment.

Due to the surprising selective toxicity of aqueous N-halohydantoin compositions, the compositions can be employed in many biocidal applications wherein the composition does or may contact desired higher order plants. 15 Accordingly, greenhouse surfaces susceptible to microorganism development may be cleaned with a solution of N-halohydantoin without undue concern as to whether any of the solution incidentally contacts the higher order plants 20 growing in the greenhouse. Moreover, N-halohydantoin can be incorporated into irrigation water to control the growth of microorganisms in the water, on the irrigation equipment and on surfaces contacted by the water without harming the plants to be irrigated.

25 It has also been found that because of the selective phytotoxicity characteristic, N-halohydantoin can be incorporated into irrigation water or otherwise applied directly to plants or to the growth medium in which plants are rooted to treat the plants, to control microorganism 30 development in, on and around the plants and to control certain plant diseases, without harming the plants. Also surprisingly, it has been discovered that treating growing

plants with N-halohydantoin and then harvesting the plants, or their fruit or seeds, results in harvested plants, fruit or seeds that do not rot or spoil as early as do harvested untreated plants, or fruit or seeds from untreated plants.

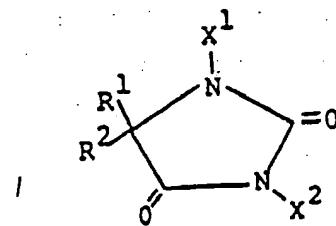
5 It further has been found that the benefit of delayed rotting or spoiling also can be achieved by applying N-halohydantoin composition directly to the harvested plants, fruit and seeds.

In addition, it has been found that the relatively low water solubility of N-halohydantoins avoids the formation of a highly concentrated phytotoxic solution. However, the concentration necessary for inhibiting microorganism development is so low that the low solubility of N-halohydantoin does not present a significant obstacle to 15 production of a solution effective in killing microorganisms. In fact, even solutions of low N-halohydantoin concentration have been found to be dramatically effective in killing microorganisms. Therefore, N-halohydantoin practically self-regulates for the appropriate concentration range, and it is essentially unnecessary to provide expensive pumps and other mechanical parts for introduction 20 of N-halohydantoin into a water system, or to introduce the biocide in a meticulously regulated manner to carefully control the N-halohydantoin concentration therein.

25 It also has been found that incorporating N-halohydantoin in a circulating water system, such as an evaporative cooler or humidifier, located in a greenhouse or otherwise located in close proximity to desired plants or other organisms, keeps the system substantially free of 30 unwanted microorganisms but does not harm the desired plants or other organisms in the environment. Moreover, it is believed that the atomized treated water propelled from

the cooler or humidifier and contacting surfaces and plants and other organisms in the environment improves the sanitation of the environment.

Preferably, the N-halohydantoin of this invention 5 is an N,N'-dihalohydantoin compound, more preferably a 1,3-dihalohydantoin corresponding to the formula:



where R<sup>1</sup> and R<sup>2</sup> are independently selected from among hydrogen and alkyl, and X<sup>1</sup> and X<sup>2</sup> are independently selected from among fluorine, chlorine, bromine, and iodine. Where R<sup>1</sup> and/or R<sup>2</sup> are alkyl, they may for example, comprise methyl, ethyl, n-propyl, isopropyl, n-butyl, or n-pentyl. Generally, it is preferred that the constituents comprising R<sup>1</sup> and/or R<sup>2</sup> contain not more 15 than about 5 carbon atoms. Preferred N-halohydantoins are N-halogenated dialkylhydantoins, especially N-halogenated dimethylhydantoins. Particularly preferred N-halohydantoins include 1,3-dibromo-5,5-dimethylhydantoin, 1-bromo-3-chloro-5,5-dimethylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin, and other hydantoin derivatives.

In this invention, N-halohydantoin is incorporated in water to produce an oxidizing biocide composition. The concentration of N-halohydantoin in the composition as it is applied to inhibit microorganism development or to 25 control plant disease should be at least about one part per million, and preferably at least about 5 ppm, to be effective against microorganisms and related diseases. However,

the concentration of N-halohydantoin in the composition as the composition contacts desired higher order plants should not exceed the point at which the composition becomes phytotoxic. Nevertheless, it has been found that the concentration of N-halohydantoin, due to its low solubility, under ordinary conditions, does not exceed about 1500 ppm, at which concentration not only has phytotoxicity not been observed, but the growth of higher order plants seems to be stimulated. Thus, a biocide of N-halohydantoin concentration between about 1 and about 1500 ppm has been found effective to kill unwanted microorganisms, yet harmless to higher order plants.

The N-halohydantoin may be incorporated into a water system at any point in the system although, of course, for a non-recirculating system the biocidal activity resulting from the N-halohydantoin only occurs downstream of the point of incorporation. Moreover, as noted, due to the self-regulatory nature of the N-halohydantoin dissolution, special pumps and other mechanical parts for metering the N-halohydantoin are unnecessary, and so the incorporation of the N-halohydantoin in water can be an essentially passive operation.

Thus, for example, solid N-halohydantoin, preferably in particulate form, can be placed in a mesh bag and suspended in a stream of water or in a well of a water circulating system. Water contacting the N-halohydantoin in the bag dissolves some of the N-halohydantoin. For a stream the relationship between flow rate and effective area of contact between water and solid biocide should be such that the downstream N-halohydantoin concentration is at least 1 ppm. As noted, due to the relatively low water solubility of N-halohydantoin, the concentration of

N-halohydantoin under ordinary conditions remains less than about 1500 ppm. Ordinarily, the concentration remains between 2 ppm and 10 ppm. Preferably the concentration is between about 5 ppm and about 10 ppm. Accordingly, by this 5 essentially passive mechanism, the treated water contains a concentration of N-halohydantoin sufficient to control development of microorganisms and plant disease without harming higher order plants.

On the other hand, if so desired, N-halohydantoin 10 may be introduced into the water by means of an inexpensive standard halogenator or brominator. If a brominator is used, either the entire water stream is directed through the brominator, or a side stream is diverted, passed through the brominator and reunited with the main stream.

15 Likewise, for applications of N-halohydantoin by hose, a brominator may be connected to the hose line or N-halohydantoin may be placed in a hose attachment such as those originally intended for application of detergents and cleaning compounds.

20 There are several applications for the water so treated with N-halohydantoin. For example, the treated water can be applied to an irrigation system to clean the irrigation equipment and other surfaces, to clean or to treat the plants and the fruit and seeds they bear, to 25 treat by foliar application the plants and the fruit and seeds the plants bear, to clean a greenhouse without harming plants therein and to treat and to clean evaporative coolers or humidifiers often found in a greenhouse.

30 In a greenhouse, plants are often watered by means of a capillary mat irrigation system. In a capillary mat irrigation system, irrigation water typically is

delivered through a conduit to a water absorbent sheet of material, such as polypropylene felt. By means of the natural absorbency of the material, the water is transported through the material to the growth medium of potted 5 plants sitting on the absorbent material.

N-halohydantoin may be introduced into a greenhouse irrigation system by directing the stream of water to be used for irrigation through a brominator containing N-halohydantoin. The biocidal activity of the treated 10 water not only tends to prevent development of unwanted microorganisms that otherwise proliferate in the water and on the irrigation equipment, but also prevents the development of microorganisms that otherwise grow and coat the irrigation mat and the pots holding the plants. Thus, by 15 including N-halohydantoin in the system, clogging of the irrigation equipment and coating of the irrigation mat are avoided, and the efficiency degradation normally encountered with the irrigation system is suppressed. Also extends the useful life of the equipment. Further, such 20 treatment of the irrigation water also inhibits development of microorganisms on the floor and other surfaces in the greenhouse often contacted by irrigation water run-off.

As for the plants themselves, the cleaner water provided by this method is believed to deliver to the 25 plants via the roots thereof fewer living microorganisms that could be deleterious to the plant. Moreover, the biocidal activity of the treated water delivered to the plant is believed to inhibit microorganism development in and on the plant, and so helps prevent or control certain 30 plant diseases which could result from pathogenic microorganisms. Importantly, therefore, this method is believed to control diseases that otherwise spread quickly through

the plants in a greenhouse. Also prevents spread of disease by re-cycled greenhouse irrigation water. Yet, despite such biocidal activity of water treated with N-halohydantoin, the plant itself is not harmed by the 5 treated water. Thus, irrigation water can be treated with N-halohydantoin for all these purposes, to avoid fouling and clogging of the equipment and other surfaces and to treat the irrigated plants, without endangering the plant.

Walls, ceilings and floors in greenhouses, and 10 even filters from evaporative coolers may be cleaned in accordance with this invention by hosing down the surfaces with treated water. The biocidally treated water kills the algae and other microorganisms that develop on the surfaces and cleans far more effectively than does untreated water, 15 but treated water that splashes onto the plants in the greenhouses does not harm the plants as do other biocides such as bleach. Therefore very time consuming removal of plants from the greenhouse before cleaning is unnecessary. For this application, the water can be treated by dissolv- 20 ing N-halohydantoin in a volume of water, by inserting N-halohydantoin in the water stream, or by directing the stream, or a side stream, through a brominator containing N-halohydantoin. The greenhouse may then be quickly and easily hosed down without serious danger of harming the 25 plants hit by splashed water, deflected water, extraneous atomized sprays of water, or even misdirected streams of water.

By the method of this invention, evaporative coolers or humidifiers, whether located in a greenhouse or 30 another environment containing plants, animals, or other organisms also can be maintained substantially free of fouling microorganisms without harming plants or animals

nearby. As with the other particular applications, N-halohydantoin can be incorporated at essentially any point in the system. Advantageously, N-halohydantoin can be placed in a mesh bag in the water collecting well of the 5 circulating system. The self-regulating mechanism of N-halohydantoin discussed above tends to maintain the treated water at an appropriate concentration. In accordance with this method, the evaporative pad remains substantially free of unwanted microorganisms that otherwise 10 accumulate, while equipment, plants or other organisms contacted by atomized treated water drifting from the cooler or humidifier not only are not harmed by the treated water, but may be disinfected by the treated water. Thus, an unhealthy environment can be converted to a healthful, 15 somewhat antiseptic environment.

As with greenhouse plants, crops or plants in an outdoor nursery may be irrigated with treated water. N-halohydantoin may be incorporated anywhere in the water system as described above, and the plants irrigated with 20 the treated water by any of several irrigation methods, such as spray irrigation, trickle or drip irrigation, mist or fog irrigation, sub-irrigation, ebb-and-flow irrigation, and hydroponics. Also as with the greenhouse irrigation methods, the treated water acts to control unwanted micro- 25 organisms from developing on the irrigation equipment, as well as in or on the plants and growth medium in which the plants are rooted. The treatment thereby helps prevent certain plant diseases arising from pathogenic micro-organisms and control the outbreak and spread of such 30 diseases.

In an alternative application of the method of the invention, solid N-halohydantoin may be placed on or in

the ground near growing plants so that rain or irrigation water delivers the N-halohydantoin to the plant's roots or rhizosphere. Likewise, solid N-halohydantoin may be placed on or in the ground near implanted bulbs or seeds so that 5 rain or irrigation water delivers the N-halohydantoin to the roots or rhizosphere of plants grown from the bulbs or seeds. Or, if desired, the bulbs or seeds themselves may be treated by applying powder or granular N-halohydantoin or a slurry or solution of N-halohydantoin directly to the 10 bulbs or seeds before planting.

In still another alternative embodiment of the application of the method of this invention growing plants may be treated with the treated water or by foliar application of an N-halohydantoin powder, slurry or solution to 15 inhibit the development of unwanted microorganisms and diseases on or in the fruit or seeds of the treated plants, and to delay rotting or spoiling of the plants, fruit or seeds even after harvesting. Significantly, the treatment process of this invention not only is harmless to the 20 plants, but because ingestion of N-halohydantoin in ordinary doses is widely believed to be safe to humans, unlike many presently available herbicides and pesticides, the resulting low doses of N-halohydantoin in the harvested 25 plants, fruits and seeds appear to pose no appreciable health hazards to humans consuming them.

Due to the self-regulating quality, N-halohydantoin can also be applied to growing plants by placing solid N-halohydantoin on or in the ground near the rhizosphere of plants, and rain water or irrigation water will dissolve 30 the N-halohydantoin to the plants in appropriate dosages. If desired, the N-halohydantoin can be applied to the ground before germination of seeds or growth of bulbs, and

can even be applied to the ground while planting seeds or bulbs, thereby eliminating the need for a separate treatment step. Optionally, or in the alternative, N-halohydantoin can be added as a powder or slurry directly to bulbs or seeds before planting. It is believed that these applications of N-halohydantoin directly to the growth medium or the bulb or seed itself and transportation to the plant by rain or irrigation water is effective in controlling development of unwanted microorganisms and plant diseases without harming higher order plants.

Alternatively, or additionally, N-halohydantoin can be applied topically to plants, fruit or seeds after harvesting. The N-halohydantoin can be dissolved in water to form a treatment solution. Then, the harvested plants, fruit or seeds can be sprayed or washed with the treatment solution. Or, if so desired, the harvested plants, fruit or seeds can be dusted or coated with N-halohydantoin powder or an N-halohydantoin slurry. Regardless, the harvested plants, fruit and seeds are not harmed nor are they believed toxic to humans. Yet, microorganism development in and on the harvested plants, fruit and seeds is inhibited and so rotting and spoiling is delayed.

Thus, N-halohydantoin can be applied in conjunction with irrigation, applied as a separate treatment or incorporated in water used for other purposes to protect plants unintentionally hit by the water.

Other advantages derived from the practice of this invention will become apparent from the following description and examples:

EXAMPLE 1

Experiments were conducted to compare the effectiveness of an N-halohydantoin composition with the effectiveness of sodium hypochlorite in producing desired levels of free residual halogen in infested water. A bromo-chloro-dimethylhydantoin (BCDMH) solution was calibrated so that five drops of the solution added to distilled water (300 ml) resulted in a solution of 1 ppm BCDMH. Water samples were collected from a muddy water seepage area in a canal site. A second set of water samples was collected from a "swamp" at the bottom of an 800-foot well. The swamp water contained 0.5 ppm hydrogen sulfide, 0.8 ppm iron, 5 ppm aromatic hydroxyl compounds and probably other unknown impurities. Drops of the BCDMH solution were added to the water samples (300 ml each) and the free residual bromine in the sample measured to determine the BCDMH concentration necessary to produce 0.6 ppm free residual Br<sup>-</sup> in the sample. The results were compared to the sodium hypochlorite concentration necessary to produce 0.6 ppm free residual Cl<sup>-</sup> in the sample. The Cl<sup>-</sup> concentration was measured with a standard Hach test kit. The Br<sup>-</sup> concentration was measured with a similar test kit. The results were as follows:

|                               | <u>Canal Water</u> | <u>Swamp Water</u> |
|-------------------------------|--------------------|--------------------|
| 25 Total NaOCl Added          | 5.6 ppm            | 4.2 ppm            |
| Free Residual Cl <sup>-</sup> | 0.6 ppm            | 0.6 ppm            |
| Total BCDMH Added             | 4.0 ppm            | 3.4 ppm            |
| Free Residual Br <sup>-</sup> | 0.6 ppm            | 0.6 ppm            |

Thus, about 23% to 40% more sodium hypochlorite than BCDMH was required to produce the same level of free residual halogen.

EXAMPLE 2

Chrysanthemums and gladioli were planted in four 50-foot plots under full-bed culture in EauGallie fine sand. The plants were irrigated by drip irrigation. One week later, BCDMH was introduced into the irrigation water of two of the 50-foot plots. The BCDMH was introduced to the irrigation water by mixing 9% aqueous BCDMH mixture (71 gal.) with water (4000 gal.). The 4071 gallons of total solution were applied to the two 50-foot plots (about 11 acre inches of irrigation) over almost ten weeks. Residual Br<sup>-</sup> concentration in the water collected from the end of the drip tube during operation was 2 to 2.5 ppm. The following results, showing no adverse effect on either chrysanthemum or gladiolus production, were obtained:

## 15 Chrysanthemums:

|                | <u>Weight/Plant (lbs.)</u> | <u>No. of Plants</u> |
|----------------|----------------------------|----------------------|
| Untreated Plot | 3.6                        | 100                  |
| Treated Plot   | 3.8                        | 100                  |

## Gladiolus:

| 20             | <u>No. of Stems</u> | <u>No. of Florets<br/>Per Stem</u> |
|----------------|---------------------|------------------------------------|
| Untreated Plot | 55                  | 14.2                               |
| Treated Plot   | 49                  | 14.6                               |

25 No significant difference in microorganism development was apparent between the tubes carrying treated water and those carrying untreated water, but it is believed that the duration of the trial was too short for any significant difference to appear.

EXAMPLE 3

Two sets of Yellow Mandalay chrysanthemums (thirty plants per set) were grown and irrigated by sub-irrigation mats. The plants were fertilized with six 5 ounces of Osmocote per cubic foot of growing medium. One set of plants (control) was not treated with biocide. For the other set of plants (test), BCDMH was injected into the irrigation system at a rate of about 2 to 4 ppm. Bromine levels of the test and control mats were measured daily and 10 the bromine level was maintain 2 to 4 ppm higher than the level of the control. About eleven weeks after planting, leaf samples were collected and analyzed. Table 1 shows 15 levels (in percent by weight) of various nutrients (nutrients for which the fertilizer was the only direct supply) found in the leaves (and compared with desired levels):

While the test samples showed lower concentrations of some nutrients, the experiments were not conducted for such analysis and fertilization was not controlled. Thus, these results are not believed significant in distinguishing the effects of BCDMH on nutrient uptake. The 20 plants were then evaluated for phytotoxicity. There was no observable phytotoxicity. The plant heights were measured, but no difference was observed between the heights or growth between the treated plants and the control plants.

25 While considerable algae growth had developed on the mat and fungus gnats had become a problem in the control set, there was no algae growth on the treated mat. Three weeks later, algae growth still had not appeared on the treated mat.

The experiment was repeated with exacum instead of chrysanthemums. Table 2 shows results from the foliar analysis were obtained:

TABLE 1

|         | <u>N</u> | <u>P</u> | <u>K</u> | <u>Ca</u> | <u>Mg</u> | <u>Mn</u> | <u>Fe</u> | <u>B</u> | <u>Cu</u> | <u>Zn</u> | <u>Al</u> | <u>Na</u> |
|---------|----------|----------|----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|
| Control | 3.42     | 0.23     | 4.1      | 2.2       | 0.64      | 339       | 111       | 20       | 7.7       | 181       | 34        | 25        |
| Test    | 3.32     | 0.12     | 1.6      | 1.0       | 0.39      | 208       | 54        | 11       | 4.6       | 126       | 22        | 21        |
| Desired | 4.5      | 0.4      | 4.0      | 1.0       | 0.3       | 30+       | 30+       | 30       | 5.0       | 30+       | -         | -         |

TABLE 2

|         | <u>N</u> | <u>P</u> | <u>K</u> | <u>Ca</u> | <u>Mg</u> | <u>Mn</u> | <u>Fe</u> | <u>B</u> | <u>Cu</u> | <u>Zn</u> | <u>Al</u> | <u>Na</u> |
|---------|----------|----------|----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|
| Control | 4.32     | 0.30     | 1.21     | 0.75      | 0.69      | 229       | 87.9      | 39       | 4.7       | 49.7      | 20.9      | 8626      |
| Test    | 4.24     | 0.37     | 0.89     | 0.83      | 0.80      | 222       | 92.7      | 47.6     | 5.1       | 70.6      | 23.1      | 9376      |
| Desired | 4.5      | 0.4      | 4.0      | 1.0       | 0.3       | 30+       | 30+       | 30       | 5.0       | 30+       | -         | -         |

While the test samples showed lower concentrations of some nutrients, the experiments were not conducted for such analysis and fertilization was not controlled. Thus, these results are not believed significant in distinguishing the 5 effects of BCDMH on nutrient uptake. Moreover, with the exacum it was noticed that of the 80 plants on the control mat, 50 had roots growing into the mat. Of the remaining 30 plants, many had roots growing out of the pot, but not yet into the mat. However, of the 77 plants on the treated 10 mat, none "stuck" to the mat or had roots growing out of the bottom of the pot. This avoidance of sticking to the mat is desirable for aesthetics and ease of handling.

#### EXAMPLE 4

The following plants received a drench of foliar 15 application of a saturated (1500 ppm) BCDMH solution:

|    | <u>Foliage Crop</u> | <u>Potted Plants</u> |
|----|---------------------|----------------------|
|    | Pilea               | Grape Ivy            |
|    | Syngonium           | Zebra Plant          |
|    | Schefflera          | Velvet Plant         |
| 20 | Pepperomia          | English Ivy          |
|    | Dieffenbachia       | Christmas Cactus     |
|    | Ficus Benjamin      | Asparagus Fern       |
|    | Neanthe Bella       | Perrywinkle          |
|    | Maranta Leuconeura  | Fibrous Begonia      |
| 25 |                     | Coleous              |
|    |                     | Impatiens            |

Applications were intermittent for three to six weeks in a greenhouse environment. No phytotoxicity was observed. In a separate experiment, the same types of plants received 30 foliar sprays containing 1500 ppm BCDMH. Plants received 3 applications of spray separated by 10 day intervals. No phytotoxicity was observed.

known. One set of seeds in each plot were uncoated. The coatings for each set and the amounts of the coating (in ounces per hundred weight) were as follows:

|    | <u>Set</u> | <u>Coating Composition</u> | <u>Amount of Coating</u> |
|----|------------|----------------------------|--------------------------|
| 5  | 1          | none                       | ---                      |
|    | 2          | Pentachloronitrobenzene    | 12                       |
|    | 3          | Phygon 27X                 | 12                       |
|    | 4          | Phygon 27X and Vitavax 30C | 10 and 3.3, resp.        |
|    | 5          | Phygon 27 and Vitavax 30C  | 10 and 3.3, resp.        |
| 10 | 6          | Phygon 29 and Vitavax 30C  | 10 and 3.3, resp.        |
|    | 7          | Phygon 27                  | 7                        |
|    | 8          | Phygon 27 and Vitavax 30C  | 7 and 3.3, resp.         |
|    | 9          | Phygon 29                  | 7                        |
|    | 10         | Phygon 29 and Vitavax 30C  | 7 and 3.3, resp.         |
| 15 | 11         | Particulate 92.5% BCDMH    | 5                        |
|    | 12         | Particulate 92.5% BCDMH    | 10                       |

The seeds were planted in various plots, with the following survival rates (in percent of planted seeds that survived) of the seeds (sets 11 and 12 were planted only in plot 3):

|    |                                  | Plots:   |          |          |          |          |          |
|----|----------------------------------|----------|----------|----------|----------|----------|----------|
|    | <u>Set</u>                       | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> |
| 25 | 1                                | 83       | 34       | 43       | 77       | 25       | 59       |
|    | 2                                | 76       | 31       | 58       | 77       | 28       | 61       |
|    | 3                                | 81       | 34       | 63       | 79       | 26       | 64       |
|    | 4                                | 82       | 26       | 69       | 73       | 48       | 63       |
|    | 5                                | 83       | 30       | 60       | 79       | 39       | 63       |
|    | 6                                | 82       | 41       | 55       | 80       | 43       | 65       |
|    | 7                                | 78       | 33       | 41       | 80       | --       | 58       |
| 30 | 8                                | 82       | 39       | 58       | 81       | --       | 65       |
|    | 9                                | 80       | 37       | 46       | 77       | --       | 60       |
|    | 10                               | 83       | 32       | 60       | 81       | --       | 64       |
|    | 11                               | --       | --       | 47       | --       | --       | --       |
|    | 12                               | --       | --       | 58       | --       | --       | --       |
| 35 | Minimum significant differences: | 5        | --       | 11       | --       | 11       | --       |

The minimum significant difference indicates the 95% confidence range within which there is no significant difference. For example, for the survival rate of set 12

The following plants were sprayed with BCDMH solutions of 1, 10, 100 and 1000 ppm in the spring:

|   | <u>Potted Plants</u> | <u>Flats</u>      |
|---|----------------------|-------------------|
| 5 | 8" Zonal Geranium    | Fibrous Begonia   |
|   | 3" Tomatoes          | Seed Geranium     |
|   | 6" Pot Mums          | Non-Stop Begonias |
|   | 4" Gebera            | Petunias          |
|   |                      | Impatiens         |

Except for occasional pinpoint burns on some flowers 10 sprayed with the most concentrated solution, no other signs of phytotoxicity were observed. Undissolved particles of BCDMH are believed to have caused the pinpoint burns. Unopened buds were not harmed.

The following plants in 4-inch pots were sprayed 15 with BCDMH solutions of 1, 10, 100 and 1000 ppm in the summer:

|    | <u>Potted Plants</u> |
|----|----------------------|
| 20 | Pteris Cretica       |
|    | Gloxinia             |
|    | African Violet       |
|    | Gerbera              |
|    | Non-Stop Begonia     |

Mild phytotoxicity symptoms were observed on open flowers at 100 and 1000 ppm.

Seeds were planted in several plots. Several sets of seeds were coated with various powder compositions. Some of the compositions comprised the commercially available products phygon, the dichrone 2,3-dichloro-30 1,4-naphthoquinone, which is a trade designation of Uniroyal, and Vitavax, a carboxin, which is a trade designation of Uniroyal. The formulas of these products are not

(58%), there is no significant difference between survival rates between 47% and 69%. Thus, it appears from the data that the BCDMH seed coating is at least as effective as the other coatings.

5 In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

Claims

## WHAT IS CLAIMED IS:

1. A method for controlling the growth of micro-organisms on a surface that is in such proximity to a higher order plant that contacting such surface with a stream of water may cause liquid water from the stream to be deflected and contact the higher order plant or the growth medium in which it is rooted, the method comprising:
  - 5 incorporating an N-halohydantoin in water to produce treated water having an N-halohydantoin concentration sufficient to inhibit the growth of microorganisms in the water or on a substrate to which the treated water is applied; and
  - 10 contacting said surface with said treated water, thereby inhibiting the growth of microorganisms on said surface, the higher order plant remaining unharmed by the N-halohydantoin contained in any of said treated water that may contact said plant or the growth medium in which said plant is rooted.
2. A method as set forth in claim 1 wherein incidental to the contacting of said surface with said treated water, treated water also contacts said plant.
3. A method as set forth in claim 2 wherein said treated water contacting said plant is in the form of atomized particles.

4. A method as set forth in claim 3 wherein said treated water is circulated through an evaporative cooler located in proximity to said plant.

5. A method as set forth in claim 1 wherein said surface comprises a greenhouse wall, ceiling or floor.

6. A method as set forth in claim 1 wherein said surface comprises an irrigation conduit.

7. A method as set forth in claim 1 wherein the N-halohydantoin concentration is between about 1 ppm and about 1500 ppm by weight.

8. A method as set forth in claim 7 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

9. A method as set forth in claim 8 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

10. A method as set forth in claim 1 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

11. A method as set forth in claim 10 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

12. A method as set forth in claim 11 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

13. A method as set forth in claim 12 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

14. A method for controlling growth of unwanted microorganisms on a surface whereby a higher order plant is not harmed, said surface being located in an environment for the growth of a higher order plant, the method comprising:

incorporating N-halohydantoin in water to produce treated water having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and

10 contacting said surface with said treated water for control of microorganisms thereon, said higher order plant being contacted with said treated water in connection with contacting said surface with said treated water.

15. A method as set forth in claim 14 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

16. A method as set forth in claim 15 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

17. A method as set forth in claim 16 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

18. A method as set forth in claim 14 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

19. A method as set forth in claim 18 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

20. A method as set forth in claim 19 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

21. A method as set forth in claim 20 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

22. A method for irrigating plants wherein disease or growth of unwanted microorganisms on or in the plants is controlled without harming the plants, the method comprising:

- 5 incorporating N-halohydantoin in water to produce treated water having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and

irrigating plants with the treated water.

23. A method as set forth in claim 22 wherein the plants are irrigated by means of spray irrigation.

24. A method as set forth in claim 22 wherein irrigation of the plant comprises transporting the treated water to the plants via a water absorbent material that is in contact with said plant or a growth medium in which it

- 5 is rooted.

25. A method as set forth in claim 22 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

26. A method as set forth in claim 25 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

27. A method as set forth in claim 26 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

28. A method as set forth in claim 22 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

29. A method as set forth in claim 28 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

30. A method as set forth in claim 29 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

31. A method as set forth in claim 30 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

32. A method for irrigating plants wherein the plants are irrigated by transportation of water to the plants by a water-absorbent material wherein growth of unwanted microorganisms on or in said material is controlled without harming the plants, the method comprising:

arranging the plants and the water-absorbent material so that water may be transported through the water-absorbent material and contact the plants or a growth medium in which they are rooted;

- 10 incorporating N-halohydantoin in water to produce treated water having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and
- 15 delivering said treated water to said water-absorbent material, thereby effecting transport of treated water to said plants on said growth medium.

33. A method as set forth in claim 32 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

34. A method as set forth in claim 33 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

35. A method as set forth in claim 34 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

36. A method as set forth in claim 32 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

37. A method as set forth in claim 36 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

38. A method as set forth in claim 37 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

39. A method as set forth in claim 38 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

40. A method for controlling disease or growth of unwanted microorganisms in a plant or its rhizosphere without harming the plant, the method comprising applying an N-halohydantoin to a growth medium in which the plant is rooted, the N-halohydantoin being dissolved in and conveyed to said rhizosphere by precipitation or irrigation water received by said growth medium.

41. A method as set forth in claim 40 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

42. A method as set forth in claim 41 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

43. A method as set forth in claim 42 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

44. A method as set forth in claim 43 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

45. A method for controlling disease or growth of unwanted microorganisms in a plant without harming the plant or inhibiting its development, the method comprising applying an N-halohydantoin to a growth medium in which a 5 seed or a bulb for the plant is implanted, the N-halohydantoin being dissolved in and conveyed by precipitation or irrigation water received by said growth medium to said seed, bulb or plant resulting from germination of said seeds.

46. A method as set forth in claim 45 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

47. A method as set forth in claim 46 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

48. A method as set forth in claim 47 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

49. A method as set forth in claim 48 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

50. A method for controlling disease or growth of unwanted microorganisms in or on a plant without harming the plant, the method comprising contacting the plant with an N-halohydantoin.

51. A method as set forth in claim 50 wherein the plant is contacted with the N-halohydantoin by:

5 dissolving N-halohydantoin in water to produce a disinfectant solution having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and applying the disinfectant solution to said plant.

52. A method as set forth in claim 51 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

53. A method as set forth in claim 52 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

54. A method as set forth in claim 53 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

55. A method as set forth in claim 51 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

56. A method as set forth in claim 55 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

57. A method as set forth in claim 56 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

58. A method as set forth in claim 57 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

59. A method as set forth in claim 51 wherein the disinfectant solution is applied to leaves of said plant.

60. A method as set forth in claim 51 wherein the disinfectant solution is applied to said plant's roots or rhizosphere.

61. A method for treating harvested plants whereby growth of unwanted microorganisms in or on the harvested plants is controlled without harming the plants, the method comprising contacting the harvested plants with 5 an N-halohydantoin, whereby rotting or spoiling of the harvested plants is inhibited.

62. A method as set forth in claim 61 wherein the harvested plants are contacted with the N-halohydantoin by:

dissolving N-halohydantoin in water to produce a disinfect- 5 ant solution having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and contacting the harvested plants with the disinfectant solu-  
tion.

63. A method as set forth in claim 62 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

64. A method as set forth in claim 63 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

65. A method as set forth in claim 64 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

66. A method as set forth in claim 62 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

67. A method as set forth in claim 66 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

68. A method as set forth in claim 67 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

69. A method as set forth in claim 68 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

70. A method for the production of harvested plants whereby growth of unwanted microorganisms in or on the plants is controlled without harm to the plants, the method comprising:

- 5 contacting growing plants with an N-halohydantoin; and harvesting said growing plants to collect harvested plants, whereby rotting or spoiling of the harvested plants is inhibited.

71. A method as set forth in claim 70 wherein the growing plants are contacted with the N-halohydantoin by:

5 dissolving N-halohydantoin in water to produce a disinfectant solution having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and contacting growing plants with the disinfectant solution.

72. A method as set forth in claim 71 wherein the growing plants are contacted with the disinfectant solution by applying the disinfectant solution as irrigation water to the growing plants.

73. A method as set forth in claim 71 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

74. A method as set forth in claim 73 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

75. A method as set forth in claim 74 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

76. A method as set forth in claim 71 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

77. A method as set forth in claim 76 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

78. A method as set forth in claim 77 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

79. A method as set forth in claim 78 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

80. A method for production of harvested fruit or seeds whereby growth of unwanted microorganisms in or on the fruit or seeds is controlled without harm to the fruit or seeds or to a plant bearing the fruit or seeds, the 5 method comprising:

contacting growing plants bearing fruit or seeds with an N-halohydantoin; and  
harvesting the fruit or seeds from the plants to collect harvested fruit seeds, whereby rotting or spoiling of the 10 harvested fruit or seeds is inhibited.

81. A method as set forth in claim 80 wherein the growing plants are contacted with the N-halohydantoin by:

dissolving N-halohydantoin in water to produce a disinfect-5 ant solution having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and  
contacting the growing plants bearing fruit or seeds with the disinfectant solution.

82. A method as set forth in claim 81 wherein the growing plants are contacted with the disinfectant solution by applying the disinfectant solution as irrigation water to the growing plants.

83. A method as set forth in claim 81 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

84. A method as set forth in claim 83 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

85. A method as set forth in claim 84 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

86. A method as set forth in claim 81 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

87. A method as set forth in claim 86 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

88. A method as set forth in claim 87 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

89. A method as set forth in claim 88 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

90. A method for controlling disease and micro-organism development in harvested plants without harm to the plants, the method comprising:

contacting growing plants with an N-halohydantoin; and  
5 harvesting said growing plants.

91. A method as set forth in claim 90 wherein the growing plants are contacted with the N-halohydantoin by:

dissolving N-halohydantoin in water to produce a disinfectant solution having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and  
5 contacting the growing plants with the disinfectant solution.

92. A method as set forth in claim 91 wherein the growing plants are contacted with the disinfectant solution by applying the disinfectant solution as irrigation water to the growing plants.

93. A method as set forth in claim 91 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

94. A method as set forth in claim 93 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

95. A method as set forth in claim 94 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

96. A method as set forth in claim 91 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

97. A method as set forth in claim 96 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

98. A method as set forth in claim 97 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

99. A method as set forth in claim 98 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

100. A method for controlling disease and micro-organism development in harvested fruit or seeds without harm to the fruit, seeds or plants bearing the fruit or seeds, the method comprising:

5 contacting growing plants bearing fruit or seeds with the disinfectant solution; and

harvesting said fruit or seeds from said growing plants.

101. A method as set forth in claim 100 wherein the growing plants are contacted with the N-halohydantoin by:

5 dissolving N-halohydantoin in water to produce a disinfectant solution having a concentration of N-halohydantoin sufficient to inhibit growth of microorganisms; and contacting the growing plants with the disinfectant solution.

102. A method as set forth in claim 101 wherein the growing plants are contacted with the disinfectant solution by applying the disinfectant solution as irrigation water to the growing plants.

103. A method as set forth in claim 101 wherein the concentration of N-halohydantoin is between about 1 ppm and about 1500 ppm by weight.

104. A method as set forth in claim 103 wherein the N-halohydantoin concentration is between about 2 ppm and about 10 ppm by weight.

105. A method as set forth in claim 104 wherein the N-halohydantoin concentration is between about 5 ppm and about 10 ppm by weight.

106. A method as set forth in claim 101 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

107. A method as set forth in claim 106 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

108. A method as set forth in claim 107 wherein the N-halohydantoin is selected from the group consisting

of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

109. A method as set forth in claim 108 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

110. A method for controlling disease or growth of unwanted microorganisms in a plant or its rhizosphere without harming the plant, the method comprising applying an N-halohydantoin to a seed or bulb for the plant and 5 planting the seed or bulb.

111. A method as set forth in claim 110 wherein the N-halohydantoin comprises an N-halogenated dialkylhydantoin.

112. A method as set forth in claim 111 wherein the N-halohydantoin comprises an N-halogenated dimethylhydantoin.

113. A method as set forth in claim 112 wherein the N-halohydantoin is selected from the group consisting of bromo-chloro-dimethylhydantoin, dibromo-dimethylhydantoin and dichloro-dimethylhydantoin.

114. A method as set forth in claim 113 wherein the N-halohydantoin comprises bromo-chloro-dimethylhydantoin.

## AMENDED CLAIMS

[received by the International Bureau on 14 March 1988 (14.03.88);  
original claims 61 and 62 amended; other claims unchanged (1 page)]

59. A method as set forth in claim 51 wherein  
the disinfectant solution is applied to leaves of said  
plant.

60. A method as set forth in claim 51 wherein  
the disinfectant solution is applied to said plant's roots  
or rhizosphere.

61. (Amended) A method for treating harvested  
plants whereby growth of unwanted microorganisms in or on  
the harvested plants is controlled without harming the  
plants, the method comprising contacting the harvested  
5 plants with an N-halohydantoin powder, whereby rotting or  
spoiling of the harvested plants is inhibited.

62. (Amended) A method for treating harvested  
plants whereby growth of unwanted microorganisms in or on  
the harvested plant is controlled without harming the  
plants, comprising:

5 mixing an N-halohydantoin in water to produce a disinfectant  
solution or slurry having a concentration of N-halohydantoin  
sufficient to inhibit growth of microorganisms; and  
washing or spraying the harvested plants with the disin-  
fectant solution or slurry.

63. A method as set forth in claim 62 wherein  
the concentration of N-halohydantoin is between about 1 ppm  
and about 1500 ppm by weight.

64. A method as set forth in claim 63 wherein  
the N-halohydantoin concentration is between about 2 ppm  
and about 10 ppm by weight.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US87/02257

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>3</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC  
 IPC(4): A01N 43/50; A01N 25/30, 25/00  
 U.S.Cl.: 514/389; 71/3, 67

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>4</sup>

| Classification System | Classification Symbols |
|-----------------------|------------------------|
| U.S.Cl.:              | 514/389; 71/3, 67      |

Documentation Searched other than Minimum Documentation  
 to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>

| Category <sup>6</sup> | Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup> | Relevant to Claim No. <sup>18</sup> |
|-----------------------|--|-------------------------------------|
| A                     | U.S., A, 3,412,021 (PATERSON) 19 November 1968, see column 1.  | 1-114                               |
| Y                     | U.S., A, 4,058,618 (OVICHINNIKOV ET AL), 15 November 1977, see the abstract.                                   | 1-114                               |
| Y                     | U.S., A, 4,167,832 (ZETTERQUIST ET AL), 18 September 1979, see abstract and columns 1 and 2.                   | 1-114                               |
| Y                     | U.S., A, 4,198,423 (RENTZEA ET AL), 15 April 1980, see the abstract.   | 1-114                               |
| A                     | U.S., A, 4,454,133 (BERKE ET AL), 12 June 1984, see the abstract.  | 1-114                               |
| A, P                  | U.S., A, 4,655,815 (JAKUBOWSKI) 7 April 1987, see abstract.  | 1-114                               |

\* Special categories of cited documents: <sup>19</sup>

- "A" document defining the general state of the art <sup>20</sup> - is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority <sup>21</sup> - is or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"S" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search: <sup>22</sup>

10 DECEMBER 1987

International Searching Authority: <sup>23</sup>

ISA/US

Date of Mailing of this International Search Report: <sup>24</sup>

12 JAN 1988

Signature of Authorized Officer <sup>25</sup>

  
 John W. Rollins

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

|   |   |       |
|---|---|-------|
| Y | G.B., B, 1,472,049 (OVCHINNIKOV ET AL) 27 April 1977, see the abstract. | 1-114 |
| A | J.P., B, 53-34923 (KENKYU) 31 March 1978 see abstract.                  | 1-114 |
| Y | S.U., A 552,973 (OVCHINNIKOV ET AL), 29 April 1977 see abstract.        | 1-114 |

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers ..... because they relate to subject matter that is not required to be searched by this Authority, namely:

2.  Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**